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Crystal structure of the α-modification of caesium gallium(III) monohydrogen triphosphate, α-$CsGaHP_3O_{10}$

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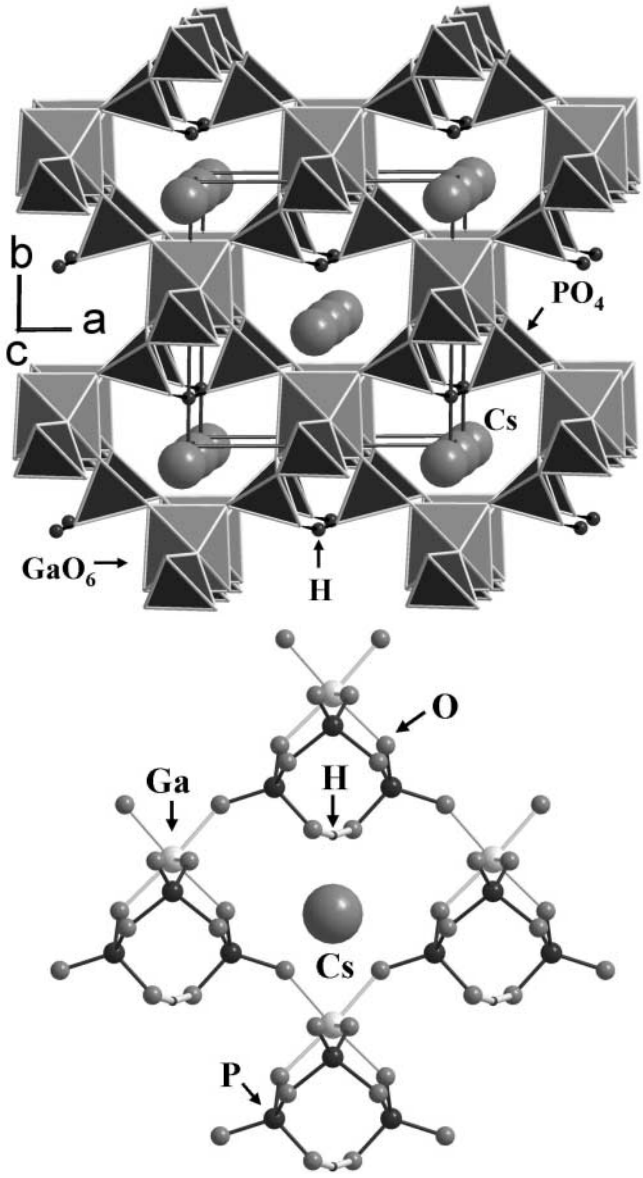

Abstract

$CsGaHO_{10}P_3$, monoclinic, $C121$ (No. 5), a = 9.061(1) Å, b = 8.7105(9) Å, c = 6.2195(8) Å, β = 111.993(6)°, V = 455.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.018, $wR_{ref}(F^2)$ = 0.046, T = 295 K.

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Source of material

The title compound was synthesized in aqueous solution by two steps. In the first step, the reaction was carried out with the mixture of $GaCl_3$(1.046 metal gallium dissolved in 5 ml 37% HCl), CsCl (2.525 g) and an excess of HCl (molar ratio Ga : Cs = 1 : 1). The mixture was heated to the boiling point. While it was cooled down and evaporated in air for several days, transparent colorless crystals were obtained. After filtering from liquid, they were identified to be $CsGaCl_4$ [1], and it was confirmed by X-ray powder diffraction. On the second step, the reaction was made with the mixture of $CsGaCl_4$ (3.44 g), $Cs(OH) \cdot H_2O$ (1.679 g) and 5 ml 85% H_3PO_4 (molar ratio 1:1:7). The starting materials were all of analytical grade. The mixture was heated (open system) to the boiling point on stove and kept heating for three days to evaporate the solvent. Three modifications of crystals of $CsGaHP_3O_{10}$ were obtained in the reaction product. The α-modification showed in block shape; 3M-modification in thick plate and 1M-modification in thin plate. All of them were colorless and transparent. The 2O-modification reported by Anisimova (1995) as III-$CsGaHP_3O_{10}$ was not found in these products indicating that it should have different synthetic conditions or a different stability temperature range.

Experimental details

The position of the H atom was determined from a difference Fourier map.

Discussion

In 1987, Chudinova et al. reported [2] a series of caesium gallium phosphate compounds, namely $Cs_2GaH_3(P_2O_7)_2$, $Gs_3Ga_3P_{12}O_{36}$ and $CsGaHP_3O_{10}$, and claimed that the formulae $CsGaHP_3O_{10}$ contains four modifications from powder diffraction data. By comparing the powder diffraction patterns of different phases, the authors assumed that phase I and III should have some common structural characteristics. Later in 1995, Anisimova et al. synthesized the modification III, reported its crystal structure and claimed that III-$CsGaHP_3O_{10}$ was the most stable one among the four modifications [3]. Although several kinds of caesium gallium phosphate structures are available [4-7], the structures of the other three modifications of $CsGaHP_3O_{10}$ have not been reported until now. Here we report one of them. According to our systematic structural researches, modifications of $CsGaHP_3O_{10}$ should belong to different polymorphs and polytypes. We name them as α-, 1M-, 2O-, 3M-modifications, respectively. The α-modification and 1M-modification belong to monoclinic system with space groups of $C2$ and $P2/n$ respectively [8]. The 2O-modification belongs to orthorhombic system with $Pca2_1$ [2].

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The crystal structures of the four $CsGaHP_3O_{10}$ modifications have a common building unit, i.e. a triphosphate [HPO_3-O–PO_2–O-HPO_3] group. In each unit, each PO_4 tetrahedron shares two further O-corners with two GaO_6 octahedra. Thus, three-membered phosphate tetrahedra groups linked with GaO_6 octahedra lead to a three-dimensional framework structure in the α-modification and a two-dimensional layer structure in the 1M-, 2O-, 3M-modifications.

In the title structure, [HPO_3-O–PO_2–O-HPO_3] groups stretch in a chiral chain mode along *c* axis and link with GaO_6 octahedra via O-corners to modification a three dimensional framework structure. It is isotypic to $CsMnHP_3O_{10}$ [9]. Caesium cations are distributed within the channels of eight-membered ring as cross-section which formed by alternating GaO_6 octahedra (4×) and phosphate tetrahedra (4×), running along the *c* axis. Caesium has coordination number of 10 with the distances from 3.033 Å to 3.667 Å. The Ga—O bond distances within the coordination octahedra range from 1.931 Å to 1.979 Å. The P—O bond distances (ranging from 1.578 Å to 1.632 Å) for bridging P–O–P oxygen are apparently larger than the P—O bond distances in the structure (ranging from 1.491 Å to 1.510 Å in PO_4 tetrahedra).

Table 1. Data collection and handling.

Crystal:	transparent colorless block, size 0.12 × 0.12 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	75.29 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7-CCD, 500 images, $\Delta\varphi = 0.6°$, 60-ω scan, $\Delta\omega = 0.6°$, $\chi = 90°$
$2\theta_{max}$:	64.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3897, 1363
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1362
$N(param)_{refined}$:	71
Programs:	SHELXL-97 [10], DIAMOND [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*a*	1/2	0.6831	0	0.05

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	2*b*	0	0.94671(2)	1/2	0.0540(2)	0.0154(2)	0.0208(2)	0	–0.0032(1)	0
Ga(1)	2*a*	0	0.61078(4)	0	0.0076(1)	0.0065(2)	0.0066(2)	0	0.0026(1)	0
P(1)	2*b*	0	0.5143(1)	1/2	0.0107(3)	0.0088(4)	0.0058(4)	0	0.0038(3)	0
P(2)	4*c*	0.81768(7)	0.32891(7)	0.1061(1)	0.0081(2)	0.0081(3)	0.0087(3)	–0.0015(2)	0.0034(2)	0.0005(2)
O(1)	4*c*	0.8349(2)	0.4551(2)	0.9508(3)	0.0118(7)	0.0091(8)	0.0102(8)	–0.0039(7)	0.0031(6)	0.0007(7)
O(2)	4*c*	0.6489(2)	0.2762(2)	0.0339(4)	0.0106(7)	0.0114(9)	0.0193(9)	–0.0061(7)	0.0052(6)	–0.0006(7)
O(3)	4*c*	0.8574(2)	0.4045(2)	0.3617(4)	0.0179(8)	0.019(1)	0.0088(9)	–0.0078(7)	0.0062(7)	–0.0018(7)
O(4)	4*c*	0.9480(2)	0.6062(3)	0.6613(3)	0.0162(7)	0.0138(9)	0.0064(7)	0.0041(7)	0.0059(6)	0.0005(7)
O(5)	4*c*	0.4376(2)	0.7013(3)	0.1440(4)	0.0178(8)	0.015(1)	0.024(1)	0.0055(7)	0.0121(8)	0.0072(7)

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